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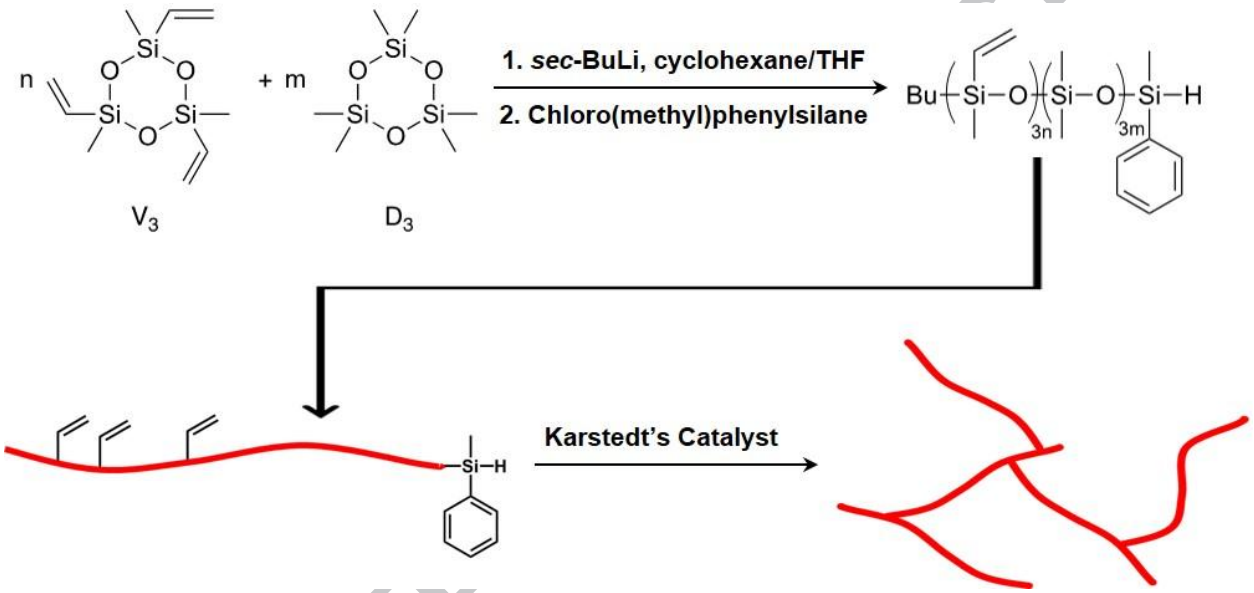
Graphical Abstract



Synthesis and Coupling of AB_x Polysiloxane Macromonomers to Form Highly Branched Polysiloxanes

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Abstract:

This work focuses on the synthesis of polysiloxane AB_x macromonomers with functional groups (A [Si-H] and B [vinyl]) incorporated on to the polymer backbone, and the coupling of these functionalities to form randomly, but highly, branched polymers. The synthesis of the AB_x macromonomers was performed by the anionic copolymerization of hexamethylcyclotrisiloxane (D_3) and 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3) monomers, followed by an end-capping/termination reaction with chloro(methyl)phenylsilane. The resulting macromonomers were coupled by a Pt(0) catalyzed hydrosilylation reaction, to yield highly branched polysiloxanes. The coupling reaction was investigated at different solution concentrations and using macromonomers with different extents of vinyl content. It was shown that a higher solution concentration resulted in higher degrees of chain coupling and branching, arising from efficient intermolecular coupling in preference to (the competing) intramolecular coupling (cyclization) reaction. Moreover, an increase in the mole fraction of vinyl monomer also resulted in higher levels of branching. With the ability to control the degree of branching, the strategy reported here provides a facile route to synthesize branched polysiloxanes (silicones) with varying flexibility and elasticity.

Keywords:

Anionic polymerization, polysiloxanes, highly branched polymers, macromonomer.

Declaration of Interest:

None.

Introduction:

Polymer architecture plays an enormous role in determining the polymer properties. Branching is known to impact the physical properties such as polymer crystallinity, the glass transition temperature and the solution and melt viscosity of polymers. Having multiple chain-ends and a branched architecture results in compact polymer structures, increased solubility and decreased viscosity.[1-3] Anionic polymerization is the optimal living chain-growth polymerization and provides control over molecular weight, dispersity (Đ), microstructure and chain-end functionality, while also enabling the synthesis of block and statistical copolymers in one-pot.[1, 4, 5] Such characteristics make anionic polymerization very suitable for the synthesis of branched polymer structures.

Polydimethylsiloxane (PDMS) is well-known for its high flexibility, low reactivity, low UV absorption, low surface energy, high gas permeability, biocompatibility and thermal stability. It is commonly used for catalysis, drug delivery, healthcare products, microfluidic devices, oil absorption and in surfactants and antifoaming agents.[6-12] All of these properties and applications of PDMS have generated significant interest in the synthesis of PDMS with branched architectures. Different methods to synthesize branched polydimethylsiloxanes have been reported in the literature.[2, 9, 13-16] In 2003, Chojnowski *et al*. reported the synthesis of star and dendritic PDMS polymers where the researchers copolymerized hexamethylcyclotrisiloxane (D_3) and 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3) monomers by anionic ring-opening polymerization (AROP) to achieve macromolecules with pendant vinyl groups.[9] These living copolymerizations were then terminated by using a reactive core containing four Si-Cl bonds which ultimately resulted in the formation of star-branched polymers. The pendant vinyl groups on the polymers were then reacted with chlorodimethylsilane *via* a hydrosilylation reaction and then these polymer chains with pendant Si-Cl functionalities were used to terminate the anionic copolymerization of other linear chains comprising of D_3 and V_3. This grafting approach facilitated the stepwise coupling of larger molecules leading to dendritic PDMS polymers.

A particularly successful coupling strategy is the macromonomer approach, where a linear polymer is synthesized with appropriate functionalities that are capable of

undergoing post-polymerization coupling reactions *via* standard organic reactions.[17-37] These macromonomers are usually synthesized by controlled or living polymerization mechanisms and bear functional groups which may be introduced during the initiation, propagation or termination steps. Our group was one of the earliest to report on the use of the macromonomer approach and previously adopted an AB_2 macromonomer approach, A and B are two different functional groups capable of reacting with each other, to synthesize highly branched (HyperMacs) polystyrenes and polybutadienes, where the A functionality was introduced by end-capping and the B functionality was introduced during the initiation.[38-40] We have also reported the macromonomer approach in the synthesis of well-defined model branched "DendriMacs" from both polystyrene and polybutadiene, long-chain branched block copolymers (HyperBlocks) and asymmetric star-branched polymers.[38, 41-44] Frey *et al*.[45] reported the coupling of AB_x polyisoprene macromonomers *via* a platinum catalyzed hydrosilylation reaction, whereby several Si-H end-functionalized polyisoprene macromonomers with varying microstructures, and therefore vinyl content, were synthesized by anionic polymerization. The resulting polymers were comprised of a mixed microstructure of both 1,4 and 1,2 (or 3,4) repeat units, the former containing an alkene bond in the polymer backbone and the latter a pendant/terminal vinyl double bond. Only the pendant double bonds were able to react during the hydrosilylation reaction. These macromonomers were then (self)coupled by a hydrosilylation reaction to form highly branched polyisoprenes and the impact of the microstructure on the coupling reaction was reported. The method reported provided a straightforward route to synthesize branched polyisoprenes. This work inspired us to develop a similarly facile procedure for the synthesis of highly (hyper)branched polysiloxanes.

Herein we report a two-step synthetic procedure for the synthesis of randomly branched polysiloxanes based on the AB_x macromonomer approach. The macromonomers were synthesized by AROP of D_3 and V_3 monomers and coupled *via* hydrosilylation reactions.

Experimental:

Materials: Tetrahydrofuran (THF) was stirred and degassed over sodium wire (Aldrich, 99.9%) and benzophenone (Aldrich, 99%), by a series of freeze-pump-thaw cycles, until

the solution turned purple, and subsequently stored under high-vacuum and the THF was distilled immediately prior to the reaction. Cyclohexane (Aldrich, ≥99.9%), toluene (Aldrich, 99.8%), hexamethylcyclotrisiloxane (Aldrich, 98%), 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (Fluorochem, >95%) and styrene (Sigma-Aldrich, ≥99%) were dried and degassed over calcium hydride (Acros Organics, 93%) by freeze-pump-thaw cycles and stored under high-vacuum. *sec*-Butyllithium (1.4 M in cyclohexane, Sigma-Aldrich), *n*-butyllithium (2.5 M in hexanes) (Aldrich), chloro(methyl)phenylsilane (Aldrich, ≥93%), butylated hydroxytoluene (BHT) (Aldrich, ≥99%) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene (Pt ~2 %, Aldrich) were used as received. Methanol (Fisher Scientific, AR grade) was used as received.

Analysis: The polymers were analyzed by nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC). All samples were prepared in $CDCl_3$ (Apollo Scientific, ≥ 99.96% D) and analyzed using a Bruker Avance 400 MHz spectrometer. The SEC results were obtained using a Viscotek TDA 302 with refractive index, light scattering and viscosity detectors. The instrument was equipped with 2 PLgel 2 x 300 mm 5 µm mixed C columns. The solvent was THF with a flow rate of 1.0 ml/min at 35 °C. Only refractive index data was used for the calculations. A conventional calibration was generated using narrow dispersity polystyrene standards obtained from Polymer Laboratories with a molecular weight range of 192 – 1,112,000 g mol^{-1}. Molecular weight analysis was carried out with OmniSEC software.

Polymer Synthesis:

Synthesis of polydimethylsiloxane-co-polymethylvinylsiloxane (PDMS-PMVS) macromonomers:

In a typical reaction (PDMS-PMVS 1), 9.86 g (44.3 mmol) of D_3 and 1.28 g (4.92 mmol) of V_3 were distilled (under vacuum) into separate flasks. 50 ml of cyclohexane was distilled into a Strauss flask containing living polystyrene chains (PSLi) to further purify the solvent. PSLi was prepared by mixing 5.00 g (48.0 mmol) styrene and 5 ml *n*-BuLi (2.5 M in hexanes) in 20 ml cyclohexane. 40 ml and 10 ml of cyclohexane were subsequently vacuum-distilled from the PSLi into the flasks containing the D_3 and V_3 monomers, respectively, followed by the injection of 100 µl (0.25 mmol) and 20 µl (0.05

mmol) respectively of *n*-BuLi solution to purify the each of monomers. The purified monomer solutions were then distilled into the reaction flask. The polymerization was initiated by the injection of 1.32 ml (1.86 mmol) of 1.4 M *sec*-BuLi solution *via* a gas-tight syringe. The initiation reaction was allowed to proceed for 2 hours at room temperature after which 50 ml of THF was added to instigate propagation. The polymerization reaction was terminated after 4 hours by the addition of 700 µl (4.65 mmol) chloro(methyl)phenylsilane (MPS-Cl). The polymer was recovered by precipitation using methanol with added butylated hydroxytoluene (BHT) to prevent the oxidation of the double bonds (from V_3) in the copolymer. The feed ratio of D_3 and V_3 was varied to produce two macromonomers with different compositions. The target molecular weight was 6000 g mol^{-1} for both copolymerizations.

PDMS-PMVS 1; Yield 81%; (^{1}H NMR) 11 mol % V_3, M_n 5300 g mol^{-1}, degree of end-capping 81 %; (SEC) M_n 7200 g mol^{-1}, M_w 8900 g mol^{-1}, Đ 1.25.

PDMS-PMVS 2; Yield 78%; (^{1}H NMR) 22 mol % V_3, M_n 10200 g mol^{-1}, degree of end-capping 78 %; (SEC) M_n 9600 g mol^{-1}, M_w 12700 g mol^{-1}, Đ 1.32.

^{1}H NMR ($CDCl_3$): 0.04-1.15 ppm ($C\mathbf{H}_3)_2SiO$, 0.15-0.20 ppm ($C\mathbf{H}_3)(CHCH_2)SiO$, 0.45 ppm ($C\mathbf{H}_3)(Ph)SiH$, 0.50-0.61 ppm ($CH_2CH_3)(CH_3)C\mathbf{H}$-SiO, 0.88-0.99 ppm ($CH_2C\mathbf{H}_3)(C\mathbf{H}_3)CH$-SiO, 1.10-1.20 ppm ($C\mathbf{H}HCH_3)(CH_3)CH$-SiO, 1.50-1.60 ppm ($CH\mathbf{H}CH_3)(CH_3)CH$-SiO, 5.12 ppm (Si-**H**), 5.68-6.11 ppm ($CH_3)(C\mathbf{H}C\mathbf{H_2})SiO$, 7.33-6.64 ppm Ar-**H** (MDS).

Coupling of AB_x macromonomers:

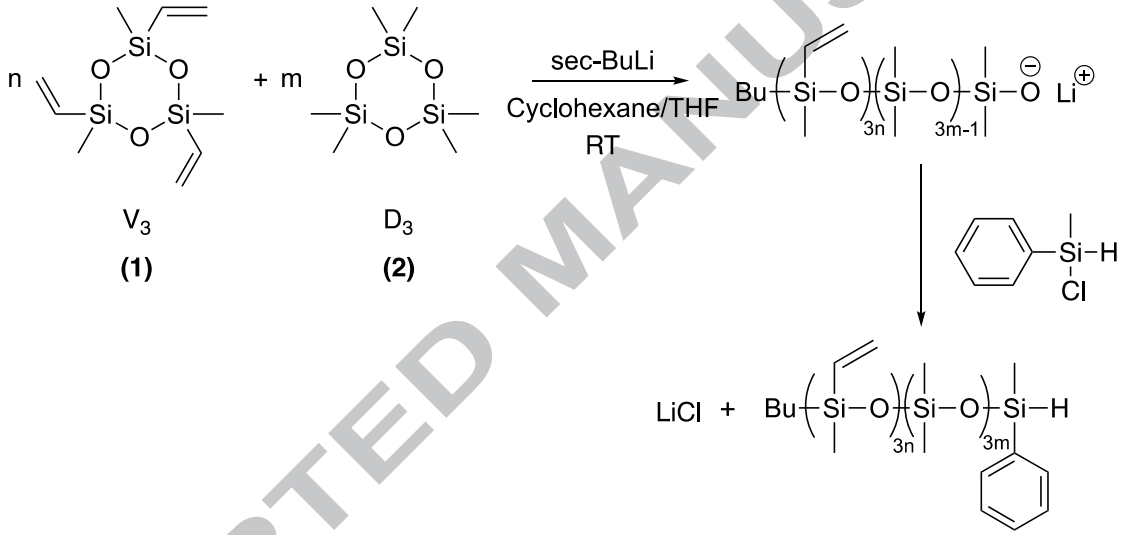
In a typical example, 1 g of PDMS-PMVS 1 copolymer (11 mol% V_3) with M_n 7200 g mol^{-1} was dissolved in 0.6 g dry toluene to form a 60% w/w concentration. The mixture was heated to 100 ^{o}C before the injection of 160 µl (4% by mol with respect to the number of moles of polymer chains) of 2% platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst in xylenes, under N_2 atmosphere. The reaction was stirred under reflux for 2 hours before cooling to room temperature. The product was recovered by precipitation using 25 ml methanol containing a small amount of butylated hydroxytoluene. PDMS-PVMS 1 copolymer was subjected to the same procedure at

varying solution concentrations, 20%, 40%, 60%, 80% (w/w) and in the bulk. PDMS-PVMS 2 was coupled at 60% (w/w) concentration.

^{1}H NMR ($CDCl_3$): 0.04-1.15 ppm ($C\mathbf{H}_3)_2SiO$, 0.15-0.20 ppm ($C\mathbf{H}_3)(CHCH_2)SiO$, 0.27-0.50 ppm ($O(Ph)(C\mathbf{H}_3)SiC\mathbf{H}_2C\mathbf{H}_2Si(CH_3)O$), 0.50-0.61 ppm ($(CH_2CH_3)(CH_3)C\mathbf{H}$-SiO, 0.88-1.00 ppm ($CH_2C\mathbf{H}_3)(C\mathbf{H}_3)$CH-SiO, 1.04-1.25 ppm ($C\mathbf{H}HCH_3)(CH_3)$CH-SiO, 1.50-1.60 ppm ($CH\mathbf{H}CH_3)(CH_3)$CH-SiO, 5.56-6.22 ppm ($CH_3)(C\mathbf{H}C\mathbf{H_2}$)SiO, 7.33-7.54 ppm Ar-**H** (MPS).

Results and Discussion:

The synthesis of the macromonomers:



V_3 (1) D_3 (2)

Scheme 1: Synthesis of Si-H end-functionalized PDMS-co-PMVS polymer.

Well-defined AB_x polysiloxane macromonomers, where A and B represent Si-H and the vinyl groups of V_3, respectively, were prepared by AROP of D_3 (**1**) and V_3 (**2**) monomers (Scheme 1). The anionic polymerization of 6-membered cyclic siloxanes is driven by ring strain of the monomers arising from the steric hindrance of the R groups on the silicon atoms. V_3 monomer is more strained than the D_3 because of the bulkier vinyl groups and this results in greater tendency for V_3 monomer to be polymerized. The reactivity ratios of V_3 and D_3 monomers were previously reported as 17.8 and 0.036 at 25 ^{o}C in THF, respectively.[9, 46] These reactivity ratios mean that V_3 shows a very strong tendency to homopolymerize whereas D_3 shows a strong tendency to

copolymerize. As such, the resulting copolymers would be far from random and an equimolar feed ratio would lead to a block-like sequence.[46] In the current study, the V_3 mole fraction in the feed was low (c. 10 – 20%) with the expectation that the V_3 would not exist as a block towards one end of the chain but it is still likely that the distribution of V_3 will be far from random and more likely to be clustered towards the α-chain end. This in turn will have an impact on the nature of the chain branching and rather than leading to a randomly branched structure, will likely result in branch points which are closer to one chain end – see Scheme 2. A mixture of the purified monomers was prepared in dry cyclohexane under standard high vacuum conditions. The polymerization was initiated with *sec*-butyllithium. THF was distilled under vacuum into the polymerization mixture to commence propagation. THF is required to inhibit the aggregation of siloxane anion around the lithium counterion which occurs in non-polar solvents. The polymerization reactions were terminated with chloro(methyl)phenylsilane after 4 hours. This end-capping agent was chosen as the phenyl group would enable facile analysis of the degree of end-capping by ^{1}H NMR spectroscopy.

Table 1: Molar mass, dispersity, degree of end-capping and yield of the macromonomers.

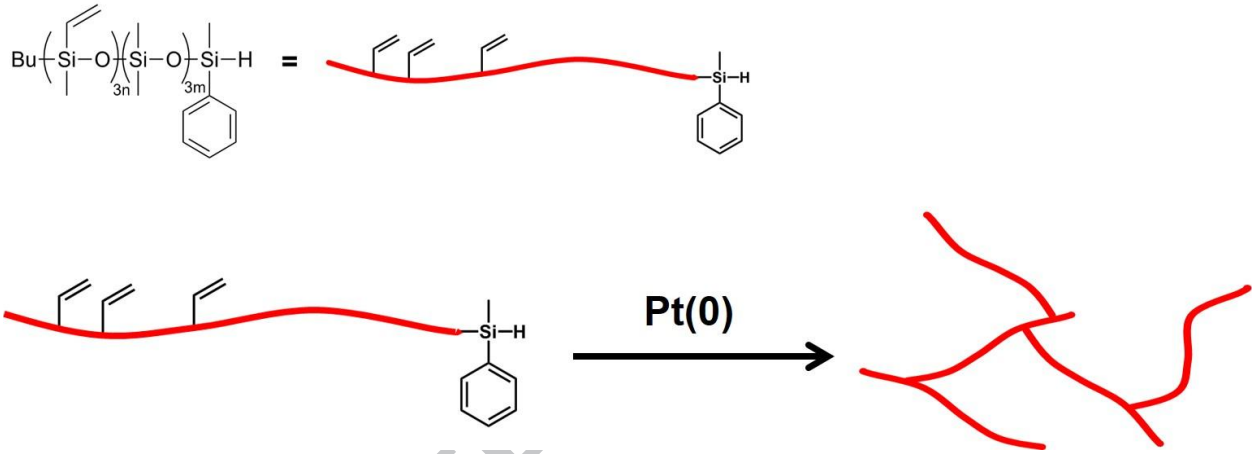
Polymer	Mol Fraction V_3 (%)	Molar Mass (g mol^{-1})			Đ	Degree of End-capping (%)	Yield (%)
		M_n [a]	M_w [a]	M_n [b]			
PDMS-PMVS 1	11	7200	8900	5300	1.25	73	81
PDMS-PMVS 2	22	9600	12700	10200	1.32	75	78

a – SEC (THF, polystyrene standards, conventional calibration), b – calculated from ^{1}H NMR ($CDCl_3$)

The mole fraction of V_3 in each copolymer, along with molar mass data obtained by both size exclusion chromatography (SEC) and NMR spectroscopy and the extent of end-capping, are reported in Table 1. A discussion of how the V_3 mole fraction and extent of end-capping was calculated from NMR data is provided in the Supporting Information (SI). All SEC analysis was performed in THF using a conventional calibration constructed using polystyrene standards (see Experimental). The low *dn/dc* of the PDMS in THF resulted in peaks of relatively low intensity meaning that analysis by triple detection was not possible. Analysis using a conventional calibration relative to polystyrene standards will result in inaccurate data and as such the molar mass (M_n)

obtained using NMR spectroscopy will be the most accurate M_n. However, despite the associated error in the molar mass data provided by SEC, the dispersity data is expected to be accurate. Dispersity values were a little high for a typical carbanionic polymerization but this is probably a result of known back-biting reactions that compete with propagation of cyclic siloxanes at high levels of conversion.[6-8, 47-51] Two copolymers were prepared with compositions comprising 11 mol% and 22 mol% V_3, respectively. In light of the competing back-biting reactions, the extent of chain-end functionalization was reasonable.

Synthesis of the highly branched polysiloxanes:



Scheme 2: The coupling of AB_x macromonomers *via* hydrosilylation reaction by using Pt(0) to obtain randomly branched polysiloxanes.

Hydrosilylation is a well-used reaction in both organic and polymer chemistry. The previous work of Frey *et al*.[45] suggested that some coupling would be observed with our AB_x polysiloxane macromonomers (Scheme 2). However, the extent of branching was a matter of speculation. One of the main aims of this work was to explore the conditions which would lead to the highest degree of chain branching and two variables were investigated; namely macromonomer solution concentration and the mole fraction of V_3 in the macromonomers. The former variable is relevant since macromonomer solution concentration will impact the ratio of intermolecular chain coupling and intramolecular chain cyclization and the latter variable is relevant since the mole fraction of V_3 will determine the value of 'x' in the AB_x macromonomer.[39] Therefore, a series of experiments were conducted to find the optimal conditions. Since one target of this

method was to limit the amount of expensive V_3 units in the macromonomer, the experiments exploring different macromonomer solution concentrations, were run on the PDMS-PMVS 1 macromonomer. The hydrosilylation reaction was performed at 20%, 40%, 60%, 80% (w/w) solutions and in the bulk. In most cases, the reaction was carried out in duplicate and, in some cases, in triplicate. The SEC traces of the resulting polymers are shown in Figure 1 and the molar masses are reported in Table 2.

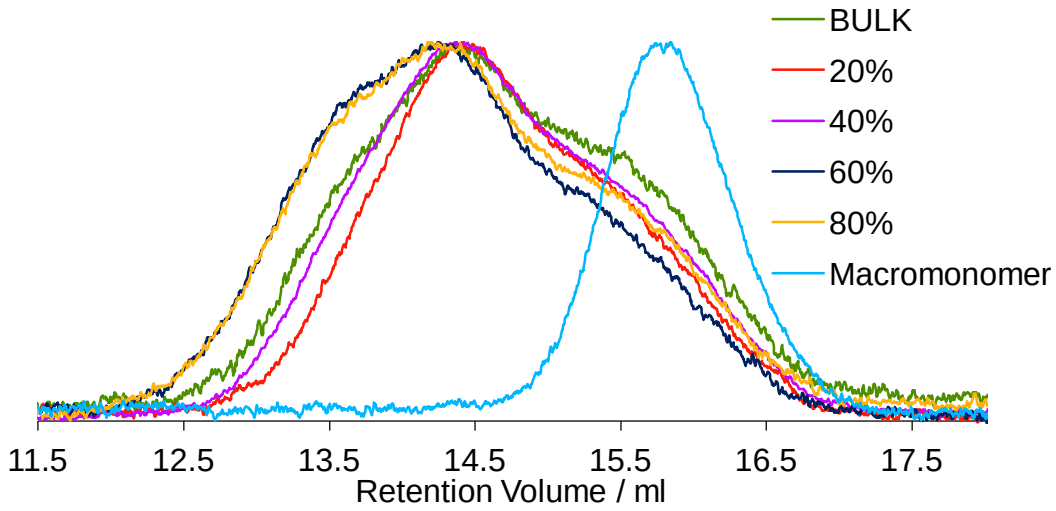


Figure 1: The SEC traces (viscometer detector) obtained from the first set of hydrosilylation reactions run at bulk (green), 20% (red), 40% (purple), 60% (blue) and 80% (yellow) weight for weight. The macromonomer is shown in blue.

The progress of the concentration optimization experiments was followed by NMR spectroscopy. In all cases, complete removal of the Si-H functionality and the broadening of the other end-capping group protons, Si-CH_3 and Si-Ph, were observed (see Figure S2, Supporting Information) as evidenced by the complete disappearance of the signal at 5.12 ppm, ascribed to the Si-H proton (H_m – Figure S1), and the broadening of the peaks at 0.45 ppm and in between 7.33-6.64 ppm, attributed to H_i and H_l, H_k, H_j, respectively. Therefore, it can be assumed that the reactions went to completion. An arising question was, however, whether the hydrosilylation reactions occurred in an intramolecular or an intermolecular fashion. It can be seen from SEC data in Table 2, that the number-average molar mass values of the branched polymers are only 2-3 times that of the macromonomer. However, assuming that the resulting polymers are indeed branched, the use of a conventional calibration (SEC) constructed

from linear standards will underestimate the actual molar mass, due to the well-known fact that branched polymers have a smaller hydrodynamic volume than linear polymers of the same molar mass. Branched polymers therefore elute later than their linear analogues and thus appear to have a lower molar mass. The reported M_w values of the resulting polymer are up to five times that of the macromonomer, which again will be an underestimate of the true M_w value, but suggesting nonetheless, a reasonable degree of chain coupling and a branched architecture. Moreover, the resulting polymers have a rather broad dispersity, between 2.0 and 2.8, which is not unexpected for the coupling of AB_x macromonomers.[45]

Table 2: Molar mass data for branched polymers obtained by the hydrosilylation coupling experiments at varying macromonomer solution concentration using PDMS-PMVS 1; M_n 7200, M_w 8900, Đ 1.25 (SEC THF, PS conventional calibration).

Macromonomer Concentration % (w/w)	Molar mass (g mol^{-1})			Averages of the molar masses (g mol^{-1})		
	M_n	M_w	Đ	M_n	M_w	Đ
20 (1)	14800	28100	1.90	14100	28050	2.00
20 (2)	13400	28000	2.10			
40 (1)	15500	32300	2.09	14550	30700	2.11
40 (2)	13600	29000	2.13			
60 (1)	20200	43600	2.16			
60 (2)	17000	44000	2.59	18000	42300	2.37
60 (3)	16800	39400	2.35			
80 (1)	14300	42600	2.97			
80 (2)	14800	43500	2.94	14700	41300	2.82
80 (3)	14900	38000	2.55			
BULK	16300	41700	2.56	16300	41700	2.56

Despite the inaccuracies in SEC data alluded to above, the SEC data is valuable for qualitative comparisons about the degree of branching for these “randomly” branched PDMS polymers. As one may expect, reactions with different macromonomer solution

concentrations yielded varying degrees of coupling. It can be seen from the molar mass data in Table 2 and Figure 2 that an increase in concentration initially resulted in a significant increase in molar mass and therefore chain coupling/branching; higher solution concentrations will favor intermolecular chain coupling over intramolecular cyclisation. It can be seen that the reactions carried out with 60% and 80% macromonomer solution concentrations and coupling in the bulk behaved in similar a manner and clearly outperformed the reactions carried out at lower concentrations. Concentrations of 60% and 80% can be regarded as the best performing reactions. In these cases the M_w of the resulting branched polymer is approximately five times the M_w of the linear macromonomer, suggesting that five linear macromonomer chains have been coupled and the high dispersity inevitably means some branched molecules will have a considerably higher degree of coupling. It is also worth recalling that SEC analysis has been carried out using a conventional calibration with linear polystyrene standards. Although the error arising from using polystyrene calibrants for PDMS polymers is a constant error for both linear PDMS macromonomers and branched polymers, the fact that branched polymers have a more compact structure and a smaller hydrodynamic volume than linear polymers of the same molar mass, means that the molar mass values obtained for the branched polymers may significantly underestimate the degree of branching. However it should also be noted that the SEC traces in Figure 1 also indicate a fraction of unreacted linear macromonomers in each case. This is evident by the residual shoulder at approximately 15.8 ml retention volume, which is coincident with the retention volume of the macromonomer, also included in Figure 1 for clarity. The samples obtained from the coupling reactions at 60% and 80% (w/w) concentrations also have shoulders at the retention volume of 12.5-13.5 ml, where the molar mass of polystyrene standard appears to be in the range of 120000-140000 g mol^{-1} – clearly there these branched polymers contain a very high molar mass fraction.

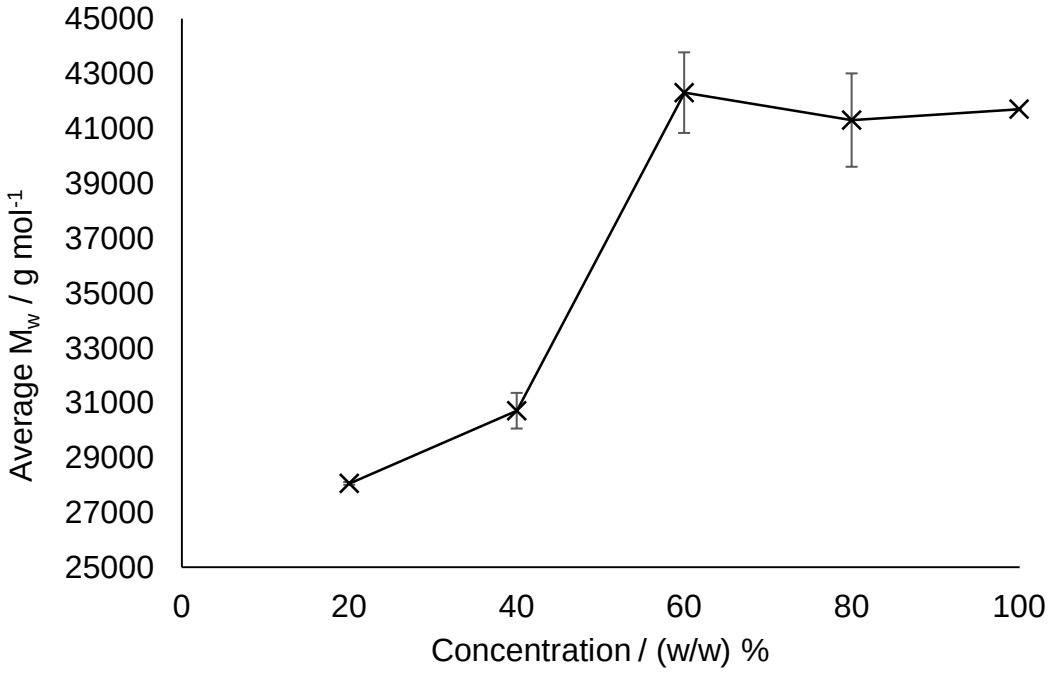


Figure 2: A plot of the average M_w (from Table 2) of the coupled polymers versus macromonomer solution concentration.

It would an oversimplification to assume that the presence of residual linear chains is due the incomplete end-functionalization of chains. Whilst it is true that NMR analysis indicates that approximately 25% of chains were not successfully end-capped with the silane functionality, that does not in itself prevent such chains from becoming incorporated into branched molecules. Such chains still possess multiple vinyl groups which allow them to take part in coupling reactions. Moreover, the overwhelming majority of branched polymers made by such strategies – *i.e.* the coupling of AB_x macromonomers do not result in the complete consumption of macromonomer.[39, 40, 45] For subsequent reactions, it was decided to use a solution concentration of 60% (w/w), to explore the impact of copolymer composition. It was anticipated that when there is a higher mole fraction of V_3 monomer in the copolymer, the result might be a higher degree of coupling and higher resulting molecular weights. This is in turn might lead to higher viscosity and the higher viscosity at 80% (w/w) might start to inhibit the coupling reaction. Frey *et al*. used 50% solution concentration and bulk for all their coupling reactions, although the authors did not provide any justification for this choice

of 50% concentration.[45] Results of the coupling reactions of copolymers with varying copolymer composition are shown in Table 3 and Figure 3.

Table 3: Data illustrating the impact of copolymer composition on extent of coupling at 60% macromonomer solution concentration (SEC THF, PS conventional calibration).

Polymer	Mol % V_3	Molar mass of macromonomer (g mol^{-1})			Molar mass of coupled polymer (g mol^{-1})			DP_w
		M_n	M_w	Đ	M_n	M_w	Đ	
PDMS-PMVS 1	11	7200	8900	1.25	18000	42300	2.37	4.8
PDMS-PMVS 2	22	9600	12700	1.32	25700	91600	3.56	7.2

Given the different composition and molar mass of the two macromonomers, a direct comparison of the molar masses of the coupled products, to infer the extent of chain coupling would be misleading. Instead, the degree of polymerization of the macromonomer (DP_w) was calculated (M_w coupled/M_w macromonomer) and used to correlate the extent of coupling with the V_3 mole fraction. This approach was previously used by Hutchings *et al* and essentially normalizes the data.[39] It can be seen that an increase in the mole fraction of V_3 and therefore the concentration of vinyl 'B' functionalities does result in a significant increase in the apparent molar mass and degree of coupling. The macromonomer containing 11 mol% V_3 had a DP_w of 4.8, which rose to 7.2 as the V_3 content increased to 22 mol%. It can be seen in Figure 3 that the high molecular weight shoulder obtained with PDMS-PMVS 1 has grown and become a peak when PDMS-PMVS 2 was used for the hydrosilylation reaction. Analysis of the fraction between retention volumes 11.0 ml and 13.5 ml, indicates a molar mass of approximately 370000 g mol^{-1} (M_w) relative to polystyrene standards. The results of the current study are in line with expectations and the previous findings of Frey *et al*. who reported an increase in molar mass and branching with an increased macromonomer solution concentration (from 50% solution concentration to bulk), as the likelihood of intramolecular cyclisation reaction decreases.[45] Frey *et al*. also reported that an

increase in the 3,4 (vinyl) microstructure of the analogous polyisoprene macromonomers led to higher degrees of chain coupling, in agreement with the data reported here for 12 mol% and 22 mol% V_3 compositions.

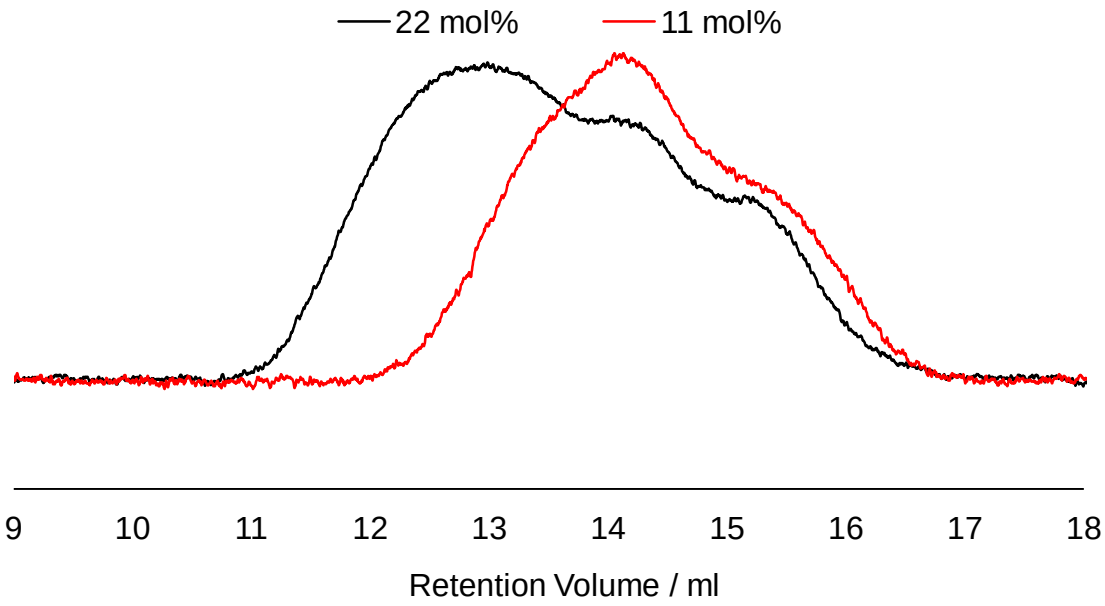


Figure 3: The SEC traces (viscometer detector) obtained from the coupling reactions of PDMS-PMVS 1 and 2 at 60% (w/w).

Conclusion:

In this paper, we have reported the synthesis of highly (randomly) branched polysiloxanes by an AB_x macromonomer approach. Initially, copolymers of D_3 and V_3 monomers were produced, to introduce some vinyl (B) groups to the polymer backbone, and the polymerizations terminated with chloro(methyl)phenylsilane to introduce Si-H (A) functionalities to the chain-end. Two PDMS-PMVS copolymers with differing V_3 mole fraction were synthesized. A series of chain coupling experiments were performed, to explore the impact of varying solution concentration on the extent of chain coupling, using the copolymer containing 11 mol% V_3. Reactions were carried out at solution concentrations between 20 and 100% macromonomer. A clear correlation was observed with molar mass, hence degree of chain coupling, increasing with solution

concentration, as intermolecular coupling was favoured over intramolecular cyclization. The optimal concentrations were determined to be 60% and 80% (w/w), however 60% was chosen for the subsequent experiments on PDMS-PMVS 2 macromonomer, to minimize any potential problems of high solution viscosity. An increase in V_3 content from 11 mol% to 22 mol% resulted in polymers with significantly higher molar masses and by implication a greater degree of branching. Overall, a facile two-step method has been demonstrated for the synthesis of randomly-branched polysiloxanes *via* the hydrosilylation coupling of AB_x PDMS-PMVS macromonomers. This strategy could (in theory) also provide an easy route to the synthesis of crosslinked silicones with the crosslinked density controlled by the composition of the AB_x macromonomer.

Data availability. The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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Supporting Information:

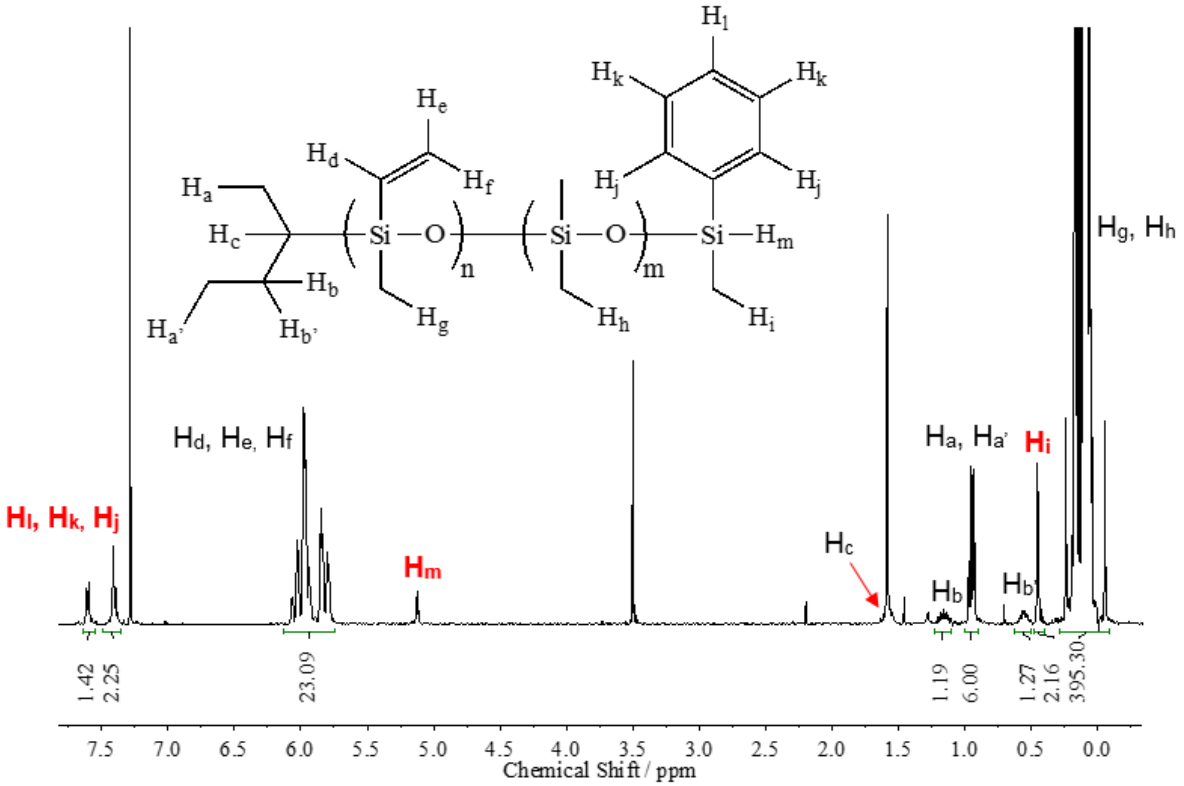

Figure S1: The ^{1}H NMR ($CDCl_3$) spectrum of PDMS-PMVS 1.

Calculation S1: Determination of M_n and composition of PDMS-PMVS 1 *via* NMR.

M_n calculation from NMR :

Molar mass of each $(CHCH_2)(CH_3)Si\text{-}O$ unit = 86.17 g mol^{-1} per unit

Molar mass of each $(CH_3)_2Si\text{-}O$ unit = 74.15 g mol^{-1} per unit

$$\text{Number of } (CHCH_2)(CH_3)Si\text{-}O \text{ units in the chain} = \frac{\text{Vinyl integral}}{\text{Protons in each vinyl unit}} = \frac{23.09 \text{ protons}}{3 \text{ protons per unit}} = 7.7 \text{ units}$$

Total molar mass of $(CHCH_2)(CH_3)Si\text{-}O$ units in the chain = 7.7 units x 86.17 g mol^{-1} per unit = 663.5 g mol^{-1}

$$\text{Number of } (CH_3)_2Si\text{-}O \text{ units in the chain} = \frac{\text{Methyl integral - Vinyl integral}}{\text{Number of protons in in each } (CH_3)_2Si\text{-}O \text{ unit}}$$

$$\Rightarrow \frac{395.30 \text{ protons - } 23.09 \text{ protons}}{6 \text{ protons per unit}} = 62.0 \text{ units}$$

Total molar mass of $(CH_3)_2Si\text{-}O$ units in the chain = 62.0 units x 74.15 g mol^{-1} per unit = 4597 g mol^{-1}

M_n of PDMS-PMVS 1 = 663.5 g mol^{-1} + 4597 g mol^{-1} = 5260 g mol^{-1} $\cong$ 5300 g mol^{-1}

V_3 composition in PDMS - PMVS 1 :

$$\text{weight \%} = \frac{663.5 \text{ g mol}^{-1}}{5260 \text{ g mol}^{-1}} \times 100 = \mathbf{13\%} \qquad \text{mol \%} = \frac{7.7 \text{ units}}{62 \text{ units} + 7.7 \text{ units}} \times 100 = \mathbf{11\%}$$

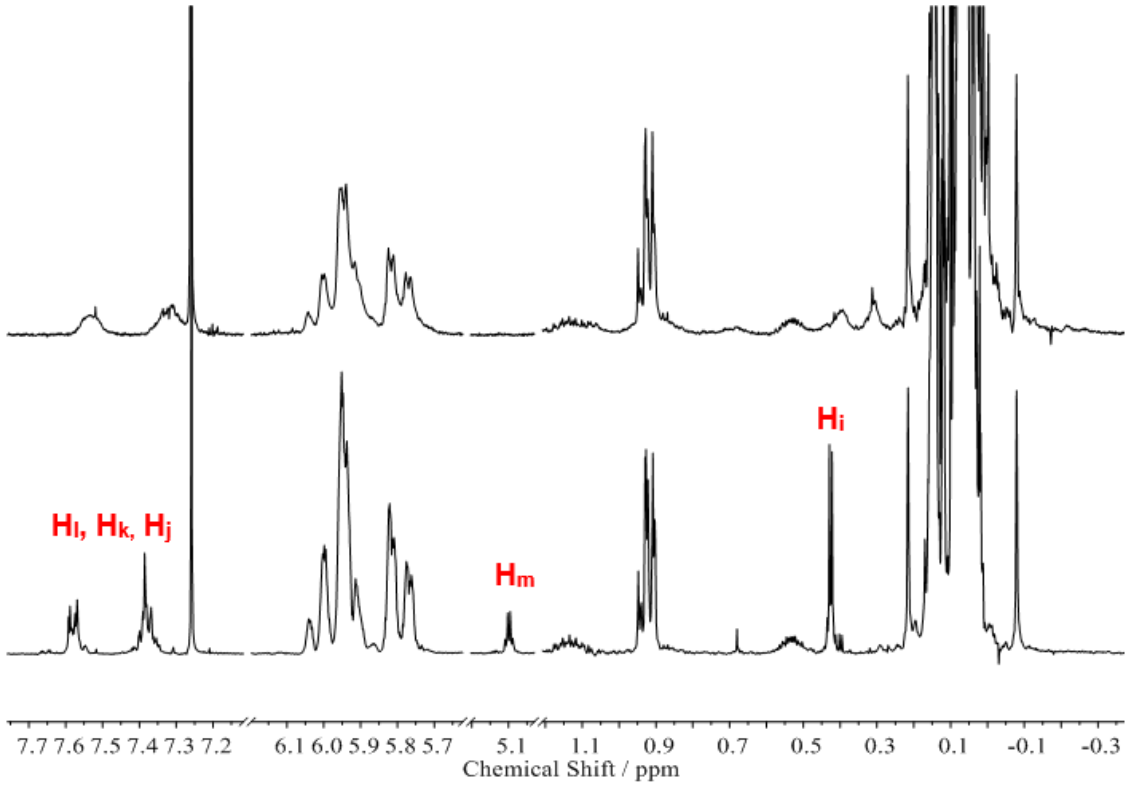

Figure S2: A comparison of ^{1}H NMR ($CDCl_3$) spectra before (bottom) and after (top) the coupling of PDMS-PMVS 1 at 20 % (w/w).

Synthesis and Coupling of AB_x Polysiloxane Macromonomers to Form Highly Branched Polysiloxanes

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Highlights

- Synthesis of AB_x polysiloxane macromonomers via anionic ring opening copolymerization
- Control over molar mass and degree of functionality via monomer feed ratio and end-functionalization
- Complex branched architecture achieved via Pt(0) catalyzed hydrosilylation coupling reaction